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COMPLETE SPECIFICATION.

Tricyclodecane Dialdehydes and Dimethylols.

I, JÜRGEN FALBE, of German nationality, of Dinslaken, Brunhildenweg 3, Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a process for the production of tricyclodecane dialdehydes and tricyclodecane dimethylols.

15 German Patent Specification No. 953,605 describes the use of rhodium-containing catalysts for the production of oxygen-containing compounds by the addition of carbon monoxide and hydrogen to olefinic compounds at an elevated pressure and in the presence of heat followed, if desired, by hydrogenation. Moreover, it is known from German Patent Specification No. 928,645 that tricyclodecane dialdehyde and its hydrogenated product, tricyclodecane dimethylol, are obtainable by hydroformylation of dicyclopentadiene. The reaction is carried out in the presence of diluents, inhibitors and stabilisers and cobalt 20 compounds yielding cobalt carbonyl hydride are used as catalysts. German Auslegeschrift No. 1,004,606 also describes the synthesis of tricyclodecane dimethylol from dicyclopentadiene by hydroformylation in the presence of a non-polar solvent followed by hydrogenation of the dialdehyde. Here again, a cobalt compound is used as the hydroformylation catalyst.

25 British Patent Specification No. 801,734 describes the use of rhodium-containing catalysts for the hydroformylation of dicyclopentadiene, these catalysts being present in solution in the reaction mixture under the reaction conditions. The unsaturated tricyclodecene monoaldehyde is obtained as the reaction product in a yield of 68% (Example 5; see also German Patent Specification No. 1,112,970). The aldehyde can subsequently

be converted into the acetal which, upon hydroformylation and subsequent hydrolysis, gives tricyclodecane dialdehyde which can be hydrogenated to form tricyclodecane dimethylol.

30 The direct production of tricyclodecane dimethylol by double hydroformylation of dicyclopentadiene followed by hydrogenation of the resultant dialdehyde is not described in that Patent Specification. While this double hydroformylation is mentioned in German Patent Specification No. 928,645, only 28% by weight of the theoretical yield, based on dicyclopentadiene, is converted into tricyclodecane dialdehyde and only 3% is converted into tricyclodecane dimethylol. While the process described in German Auslegeschrift No. 1,004,606 converts 57% to 58% of the diolefin used into tricyclodecane dimethylol, tricyclodecane monomethylol is also formed. The amount of the monomethylol is 1 mole per cent per 2.6 to 3.1 mole per cent of the dimethylol, i.e. hydrogenation of a double bond occurs to a considerable extent.

35 It is an object of the invention to provide a process for the production of tricyclodecane dialdehyde and tricyclodecane dimethylol which gives a better yield and/or improved control of the reaction.

40 According to the invention tricyclodecane dialdehydes are produced by the hydroformylation of dicyclopentadiene by reacting dicyclopentadiene in the presence of a rhodium-containing catalyst with carbon monoxide and hydrogen at a temperature above 80°C, preferably a temperature of from 100°C to 160°C, and at an elevated pressure above 30 atmospheres gauge, preferably from 50 to 300 atmospheres gauge to form tricyclodecane dialdehyde.

45 According to the invention furthermore, the hydroformylation product may be hydro-

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generated to convert the dialdehyde into the corresponding diol either after separation of the rhodium-containing catalyst by means of a conventional hydrogenation catalyst with hydrogen or without separation of the rhodium-containing catalyst and without the addition of other hydrogenation catalyst by increasing the temperature to at least 180°C with mixtures of carbon monoxide and hydrogen.

Dicyclopentadiene is obtainable in known manner, for example, by the dimerisation of cyclopentadiene. The use of a rhodium-containing catalyst directs the hydroformylation in such manner that tricyclodecane dialdehyde is preferentially produced. The rhodium-containing catalyst is advantageously used in an amount of from 1×10^{-6} to 1×10^{-2} gram-atoms of rhodium, preferably from 4×10^{-6} to 4×10^{-3} gram-atoms of rhodium, per mole of dicyclopentadiene. In one method of carrying out the invention, the catalyst is formed in the reaction mixture from rhodium sesquioxide. It is also possible, however, to add the rhodium in a different form, for example as the trichloride, nitrate or sulphate or as the metal. A soluble, catalytically active rhodium carbonyl compound is formed under the reaction conditions. It will be understood that such carbonyl compound may also be prepared before the hydroformylation and be added as such to the reaction mixture. When a carrier material is used, the rhodium compound is suitably present in an amount of 1 to 40%, based on the carrier. The molar ratio of carbon monoxide to hydrogen in the synthesis gas used is desirably adjusted to a value of between 2:1 and 1:4. The hydroformylation is preferably carried out in the presence of an inert diluent, particularly tetrahydrofuran. Other suitable diluents include, for example, methanol, ethanol, isopropanol, benzene, toluene and cyclohexane. The dicyclopentadiene may be introduced into the reaction vessel or zone after the temperature and other reaction conditions to be used in the hydroformylation have been established. The product of hydroformylation may be freed from the catalyst and solvent prior to hydrogenation. The catalyst is decomposed by pressurising the pressure apparatus and may, for example, be separated by filtration. The hydrogenation of the hydroformylation product which has been freed from the catalyst can be carried out by methods which are known *per se*. Examples of suitable hydrogenation catalysts include nickel, cobalt and chromium catalysts. Hydrogenation is carried out under conventional conditions, for example, at temperatures between 20° and 200°C. and pressures of from 1 to 400 atmospheres gauge.

However, it is particularly convenient according to the invention to carry out the hydrogenation without previous removal of the rhodium carbonyl compounds from the hydroformylation product. When operating in this manner, the hydrogenation is preferably carried out while maintaining a carbon monoxide/hydrogen molar ratio in the synthesis gas of 1:2. The reaction temperature is increased for the hydrogenation to at least 180°C and preferably to at least 200°C. The synthesis gas pressure need not, in general, be changed between the hydroformylation and hydrogenation but may, if necessary, be increased.

Upon completion of the hydrogenation, the reaction mixture is processed in conventional manner. When using the preferred mode of operation carried out with merely an increase in the temperature of the hydroformylation mixture, the contents of the autoclave are cooled after the hydrogenation and depressurised. The catalyst is then found in decomposed form and almost quantitatively as a settled powder. Cobalt catalysts readily tend to form metal mirrors and incrustations under these conditions. The rhodium precipitate may be readily removed by filtration, elutriation, etc., and re-used without further treatment. Small amounts of catalyst which are left in the raw product are decomposed when the latter is distilled but they do not pass over with the distillate to the same extent as the cobalt carbonyls do. Thus, it is a particular advantage of the invention that it provides a route towards the elimination of the necessity of using cumbersome purification methods for the removal of residual catalyst.

The process according to the invention may be carried out batchwise, or semi-continuously or continuously. Both the course of the hydroformylation and the course of the hydrogenation may be followed by sampling from the pressure apparatus followed by analysis for example, by gas chromatography.

The invention is illustrated in the following examples.

EXAMPLE 1

A suspension of 0.25 grams of Rh_2O_3 in 830 grains of benzene was heated to 130°C in an autoclave. After this temperature had been reached, synthesis gas ($\text{CO}/\text{H}_2 = 1:2$) was introduced until a final pressure of 150 kg/sq.cm was reached. A solution of 250 grams of dicyclopentadiene in 120 grams of benzene was then pumped into the autoclave. Upon completion of the addition, the pressure was increased to 200 kg/sq.cm by introducing additional water gas ($\text{CO}/\text{H}_2 = 1:2$).

Upon termination of the absorption of gas, that is, termination of the hydroformylation reaction, the temperature was increased to 130

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| 240°C. Hydrogenation of the hydroformylation product then took place, the hydrogenation proceeding to completion during the heating-up stage. The rhodium catalyst was removed from the cooled and depressurised product by filtration. The yield of raw product after separation of the benzene was 363 grams (98% of theory). The product had the following composition: | 1 : 2) was introduced until a pressure of 250 atmospheres was reached and supplemented as it was consumed. The reaction temperature was 140°C in the first tube and 200°C in the second tube. | 65 |
| 10 1.1% tricyclodecane monomethylol 1.1% hydroxymethyl tricyclodecane aldehyde | The rhodium catalyst was removed from the cooled and expanded product by filtration. | |
| 15 97.6% tricyclodecane dimethylol 0.2% thick oil (higher boiling substances) | Raw product (free from toluene) was obtained at a rate of 325 grams/hr and had the following composition: | 70 |

EXAMPLE 2

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| 20 A solution of 1 part by weight of dicyclopentadiene in 3 parts by weight of toluene was pumped through a 2 litre high pressure tube at a rate of 1 litre/hr. together with 10 ml/hr. of a catalyst suspension. The catalyst suspension consisted of a mixture of 3 parts by weight of tricyclodecane-dimethylol and 2 parts by weight of isopropanol and contained 10 grams of Rh_2O_3 per litre of carrier liquid. | 1.0% first runnings. 1.4% tricyclodecane monomethylol 93.6% tricyclodecane dimethylol 4.0% thick oil (higher boiling substances) | 75 |
| 25 At the same time, synthesis gas ($\text{CO}/\text{H}_2 = 1:1$) was introduced until a pressure of 250 atmospheres were reached are then supplemented as it was consumed. The reaction temperature was 125°C. | WHAT I CLAIM IS:— | |
| 30 In a pressure tube arranged downstream of the high pressure tube, the product was demetallised with 20% of water, based on the toluene solution used, at 125°C and 15 atmospheres using a residence time of 1 hour. | 1. A process for the production of tricyclodecane dialdehyde, which comprises subjecting dicyclopentadiene to hydroformylation with a mixture of carbon monoxide and hydrogen at a temperature above 80°C and at a pressure above 30 atmospheres gauge in the presence of a rhodium-containing catalyst. | 80 |
| 35 Raw product (free from toluene) was obtained at a rate of 317 grams/hr and it had the following composition: | 2. A process for the production of tricyclodecane dimethylols, which comprises subjecting dicyclopentadiene to hydroformylation with carbon monoxide and hydrogen in the presence of a rhodium-containing catalyst at a temperature above 80°C and at a pressure above 30 atmospheres gauge, and in a second stage hydrogenating the hydroformylation product so obtained. | 90 |
| 40 4.9% first runnings 2.8% tricyclodecane monaldehyde 88.2% tricyclodecane dialdehyde 1.9% hydroxymethyl tricyclodecane aldehyde 0.2% tricyclodecane dimethylol (from catalyst suspension) 6.0% thick oil (higher boiling substances) | 3. A process according to claim 2, in which hydrogenation of the hydroformylation product is effected with hydrogen in the presence of a hydrogenation catalyst and after removal of the rhodium-containing catalyst. | 95 |
| 45 50 EXPLANATION 3 | 4. A process according to claim 2, in which the hydrogenation of the hydroformylation product is effected with a mixture of carbon monoxide and hydrogen at a temperature of at least 180°C in the presence of the rhodium-containing catalyst. | 100 |
| 50 A solution of 1 part by weight of dicyclopentadiene in 3 parts by weight of toluene was pumped through two series-connected 2 litre high pressure tubes at a rate of 1 litre/hr. together with 10 ml/hr of a catalyst suspension. The catalyst suspension consisted of a mixture of 3 parts by weight of tricyclodecane dimethylol and 2 parts by weight of isopropanol which contained 10 grams of Rh_2O_3 per litre of carrier liquid. At the same time, synthesis gas ($\text{CO}/\text{H}_2 =$ | 5. A process according to claim 4, in which the hydrogenation is effected at a temperature of at least 200°C. | 110 |
| 55 6. A process according to any one of the preceding claims, in which the hydroformylation is effected at a temperature in the range 10—160°C and at a pressure in the range 50—300 atmospheres gauge. | 7. A process according to any one of the preceding claims, in which the rhodium-containing catalyst is used in an amount such that it contains from 4×10^{-6} to 4×10^{-3} gram atoms of rhodium per mole of dicyclopentadiene. | 115 |
| 60 8. A process according to any one of the preceding claims, in which the rhodium-con- | | 120 |

taining catalyst is formed in the reaction mixture from rhodium sesquioxide.

9. A process according to any one of the preceding claims, in which the molar ratio of carbon monoxide to hydrogen in the gas used is between 2:1 and 1:4.

10. A process according to any one of the preceding claims, in which the hydroformylation is carried out in the presence of an inert diluent.

11. A process according to claim 10, in which the inert diluent is tetrahydrofuran.

12. A process according to any one of the preceding claims, in which the dicyclopentadiene is introduced into the reaction vessel after the temperature and other reaction conditions to be used for the hydroformylation reaction have been established.

13. A process for the production of tri-

cyclodecane dialdehyde, substantially as hereinbefore described in any one of the Examples.

14. A process for the production of tricyclodecane dimethylol, substantially as hereinbefore described in Example 1 or Example 3.

15. Tricyclodecane dialdehyde whenever obtained by the process claimed in claim 1 or any one of claims 6 to 13.

16. Tricyclodecane dimethylol whenever obtained by the process claimed in any one of claims 2 to 12 and 14.

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